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**(54) Title:** GAS PHASE SILICON ETCHING WITH BROMINE TRIFLUORIDE

**(57) Abstract**

An apparatus and method for gas-phase bromine trifluoride ($BrF_3$) silicon isotropic room temperature etching system for both bulk and surface micromachining. The gas-phase $BrF_3$ can be applied in a pulse mode and in a continuous flow mode. The etching rate in pulse mode is dependent on gas concentration, reaction pressure, pulse duration, pattern opening area and effective surface area.

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## Gas Phase Silicon Etching with Bromine Trifluoride

### Field of the Invention

This disclosure relates to pulsed gas-phase
5   silicon etching in micromachining processes.  More
specifically, etching using $BrF_3$ is described.

### Background

Etching is used to form features during silicon
micromaching in micro-electromechanical systems ("MEMS").
10  The success of etching processes are characterized by the
etch rate in dimensions of thickness per unit time.  The
etch rate has dimensions of thickness per unit time.  A
high etch rate is generally desired.  However, too high
an etch rate may render a process difficult to control.
15  Common desired etch rates are in units of hundreds or
thousands of angstroms per minute.  Selectivity is the
ratio of the etch rates of silicon referenced to the etch
rate of the mask film being patterned on top of silicon.
A particular process may be quoted as having a
20  selectivity of 300 to 1,  polysilicon over oxide.  This
means that polysilicon etches 300 times faster than
oxide.  Another consideration when characterizing etching
performance is producing isotropic etches.  Isotropic
etches, meaning etches having uniform etch properties in
25  all directions, are desirable.

Silicon micromachining in MEMS often uses wet
chemical and plasma etching.  Wet chemical etching is a
purely chemical process having three steps: movement of
the etchant species to the surface of the wafer, chemical
30  reaction with the exposed film that produces soluble

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byproducts, and movement of the reaction products away from the surface of the wafer. Wet etching often yields high selectivity. However, wet etching can have serious

5   drawbacks such as poor process control and excessive particle contamination. Chemical etchants also can cause surface tension effects during drying. The meniscus force of the liquid etchant can drag on the free standing structure thereby sticking to the structure's surface

10  which can induce direct mechanical damage.

         Etching in a plasma environment has several advantages when compared to wet etching. Plasmas are easier to start and stop at precise times defining the beginning and end respectively of the etching process as

15  compared with simple immersion wet etching. Plasma etch processes are much less sensitive to small changes in the temperature of the wafer. Plasma etching involves less contaminant and no damage to fragile structures due to surface tension and stiction forces of wet etchants.

20       Plasma etching is carried out by introducing a feed gas into the chamber. The feed gas is broken down into chemically reactive species by the plasma. These chemically reactive species diffuse to the surface of the wafer and are adsorbed. The species react with the

25  exposed film. The reaction product is desorbed, diffused away from the wafer, and is transported by gas stream out of the etch chamber.

         Plasma etch processes obviate many of the wet chemical etch problems. However, plasma etching has

30  limited selectivity over silicon dioxide and nitride. The plasma environment also produces ions and soft x-ray radiation which can damage or have undesirable charging effects on the electronic devices on the substrate.

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In "Plasma-less Dry Etching of Silicon with Fluorine-Containing Compounds", Lbbotson et al, J. Appl. Phys., Vol. 56(10), 1984, p. 2939-2942; it was suggested
5 that some fluorine-containing interhalogens such as xenon difluoride can etch silicon spontaneously in the vapor phase.

Summary

10     The present invention provides an apparatus and method for gas-phase bromine trifluoride ($BrF_3$) silicon isotropic room temperature etching system for both bulk and surface micromachining. Gas-phase $BrF_3$ etching has many advantages. $BrF_3$ has a high vapor pressure at room
15 temperature. This allows ease of use and high etching rate. Gas-phase $BrF_3$ etching produces fewer damaging meniscus and stiction forces and is relatively contamination-free. Gas-phase $BrF_3$ etching produces longer undercut distance than plasma etching and produces
20 no damage to the electronics device on the substrate.

       The $BrF_3$ containing gas-phase etchant can be applied in a pulse mode and in a continuous flow mode. The $BrF_3$ gas can be diluted with another gas and this mixture can be used as the gas-phase etchant. The
25 etching rate in pulse mode is dependent on gas concentration, reaction pressure, pulse duration, pattern opening area and effective surface area.

       An apparatus and method for $BrF_3$ containing gas-phase etching is provided.

30              Brief Description of the Drawing
       These and other aspects will be described with reference to the drawings, in which:

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FIG. 1A shows a preferred etching apparatus;

FIG. 1B shows the steps in one etching pulse;

FIG. 2 illustrates etching rates at different $BrF_3$

5 pressures;

FIG. 3 illustrates silicon mass loss vs. pulse duration time for different exposed silicon areas;

FIG. 4 illustrates vertical and horizontal etching depth vs. Circular opening with varying diameters;

10      FIG. 5 illustrates vertical etching depth vs. number of pulses with different circular opening sizes;

FIG. 6 shows local loading effect and aperture opening effect;

FIG. 7 illustrates surface micromachined channels;

15      FIG. 8 illustrates surface micromachined membranes;

FIG. 9 illustrates etching length in surface micromachined channels vs. number of pulses; and

FIG. 10A and 10B compares the effect of $BrF_3$

20 dilution on surface roughness.


Description of the Preferred Embodiments

ETCHING CHEMISTRY

The literature does not suggest any efficient methods and apparatus of using $BrF_3$ gas for silicon

25 micromachining. At room temperature, $BrF_3$ is in the form of a colorless to gray yellow liquid with a vapor pressure of approximately 7.0 Torr. When compared with xenon difluoride ($XeF_2$), bromine trifluoride is easier to vaporize. $XeF_2$ has a vapor pressure of approximately 3.0

30 Torr and exists as a white power at room temperature. $BrF_3$ exists as a liquid at room temperature. This is advantageous since the etchant can be stored as a liquid. Liquids are usually easier to store in process chambers

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and to vaporize than solid powder.  $BrF_3$ has more fluorine
atoms than  $XeF_2$  per molecule.  Hence,  $BrF_3$ has a higher
etching efficiency  than that of  $XeF_2$ because fluorine
5    atoms are believed to be the active etching molecule.
$BrF_3$ etching is also cost effective when compared with the
use of  $XeF_2$ .  The cost of  $BrF_3$ etching can be as low as
10% of the cost of  $XeF_2$ etching.

      The etching mechanism of gas-phase  $BrF_3$ with
10   silicon is believed to be similar to that of other
fluorine-containing interhalogens.  The mechanism is
believed to include: (1) nondissociative adsorption of
gas-phase species at the surface of the solid being
etched; (2) dissociation of this adsorbed gas; (3)
15   reaction between adsorbed atoms and the solid surface to
form an adsorbed product molecule  $(SiF_4)$ ; (4) desorption
of the product molecule into the gas phase.  Adsorption
is the adhesion of an extremely thin layer of molecules
to the surfaces of solid bodies with which the molecules
20   are in contact.  Desorption is the release of product
molecules from a surface.

      Pure  $BrF_3$ gas can be used as a gas-phase etchant.
A mixture of  $BrF_3$ with another compound can also be used
as a gas-phase etchant.  One embodiment features diluting
25   $BrF_3$ with xenon gas to control the etching surface
roughness produced.

      The etching of silicon on the surface is believed
to be done by fluorine atoms.  The volatile products,  $SiF_4$
and  $Br_2$ , are produced as shown in equation (1):

$$4BrF_3 + 3Si = 2Br_2 + 3SiF_4 \qquad (1)$$
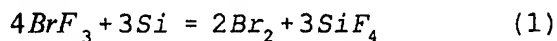
30        Assuming the etching process is limited by chemical
reaction  and the  $BrF_3$ concentration is uniform in the
reaction chamber, the number of  $BrF_3$ molecules in the

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reaction chamber, N, can be expressed as equation (2),

$$-\frac{dN}{dt} = \frac{4}{3} RA \times n_{si} \qquad (2)$$

where R is the silicon etching rate in angstrom/minute,
$n_{si}$ is the atomic density of silicon, and A is the silicon
5  opening area of the etching sample.

The $BrF_3$ etching rate is shown as a function of
silicon substrate temperature and fitted to the Arrhenius
equation in the form of equation (3),

$$R = 1.16 \times 10^{-18} \frac{N}{V} T^{1/2} Exp(-E_a / kT) \quad (Å/minute) \qquad (3)$$

where $E_a$ is the activation energy that has a value of -6.4
10  kcal/mole for $BrF_3$ at room temperature, k is the Boltzmann
constant ($1.987 \times 10^{-3}$ kcal/mole/K).  In the preferred
embodiment, T is 300K, V is $2220 cm^3$, the initial value of
N is $7.76 \times 10^{19}$.

At 1.0 Torr gas pressure and room temperature,
15  equation (3) gives an etching rate of 4.13 μm/min in the
preferred system.

By combining equation (2) and equation (3) and
solving the first-order differential equation, the number
of $BrF_3$ molecules in the reaction chamber, N, is found to
20  be an exponential function of time.  N can be converted
to the silicon mass loss as a function of etching time,
M(t) as in equation (4),

$$M(t) = M(\infty) \left[ 1 - Exp\left( -\frac{t}{\tau} \right) \right] \qquad (4)$$

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where τ is shown in equation (5),

$$\tau = C\frac{V}{A} \quad (second) \qquad (5)$$

C is a constant and has a value of $8.78 \times 10^{-2}$ s/cm for the
present system.  Equation (5) shows that the time
5  constant is inversely proportional to the silicon exposed
area A.  For the opening area of $3cm^2$, equation (5) gives
a time constant of 65 seconds.


ETCHING APPARATUS AND OPERATION

        Figure 1A shows the preferred etching apparatus
10  having a reaction chamber 110, a vapor reservoir 120,
nitrogen purge source 130, xenon dilution system 140 and
a vacuum subsystem 150.  Individual gas flow is
controlled by switching the corresponding valve 174, 178.

        Valve 176 regulates the flow of gas from the vapor
15  reservoir 120 to the reaction chamber 110.  Valve 172
regulates the flow of gas from the reaction chamber 110
to the vacuum subsystem 150.  Pressure in the vapor
reservoir 120 and reaction chamber 110 are monitored by a
pressure sensor, e.g., baratron 160 and a pressure gauge
20  170 respectively.

        The vapor reservoir 120 is used to contain certain
vapors prior to introduction into reaction chamber 110.
Gases are held at the vapor reservoir 120 to control
dilution concentration.  The vapor reservoir is coupled
25  to the reaction chamber.  A 1900cc reaction chamber 110
and a 320cc vapor reservoir 120 can process approximately
ten 4 inch wafers.  The size of the chamber and reservoir
are modified to accommodate the amount and size of the
wafers to be processed.

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In one embodiment, the reaction chamber 110, vapor reservoir 120, the interconnecting pipes, valves and any other part of the apparatus that may come in contact with

5    $BrF_3$ is covered with a layer of corrosive resistant coating. Preferably, a thin layer of Parylene-C polymer film is deposited by chemical vapor deposition at room temperature. Parylene is chemically inert and prevents $BrF_3$ corrosion of the construction materials. The organic

10   interior coating will give increased hydrophobicity to the apparatus thereby preventing undesirable condensation of gas onto the apparatus surfaces. Polyimide is another organic material that can be used as corrosive-resistant coating. Parylene-C is preferred because Parylene-C is

15   easily applied to the apparatus by chemical vapor deposition at room temperature.

Nitrogen purge 130 is used to introduce nitrogen gas which removes contaminants and water from the wafer surface.

20   A xenon dilution system 140 is used to dilute the amount of $BrF_3$ used in the reaction. A preferred dilution ratio is 1 Torr of $BrF_3$ to 99 Torr of pure xenon gas. The inventors found that $BrF_3$ has a very high reaction rate which may produce uneven etches due to a diffusion

25   limited effect. The diffusion limited effect is defined as when a reaction is limited by the time the molecules come in contact with the surface rather than the amount of reactants. Hence, some molecules may reach the surface faster than others producing an uneven etch.

30   Dilution with xenon reduces the mean free path, as a result, $BrF_3$ molecules are scattered more uniformly at a higher reaction pressure thereby resulting in a smoother surface.

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Baratron 160 is a sensitive, short range, pressure measuring device.  The baratron measures a capacitance change when the pressure changes.  The baratron is used

5  in this embodiment to measure pressure changes within a 10 Torr range.  The baratron is used as a vapor pressure sensor, positioned to measure a pressure of the vapor reservoir 120.  The pressure gauge 170 is a wide range pressure dial which is used to measure a range from 0 to

10  500 Torr in this embodiment.  The pressure gauge 170 is used as a reaction pressure sensor positioned to measure a pressure of the reaction chamber 110.

The construction materials are preferably stainless steel, brass, and nickel.  A more costly

15  material such as monel can also be used.  Monel is more $BrF_3$ corrosive-resistant than stainless steel and brass. Other $BrF_3$ corrosive-resistant materials can also be used. The inventors found a method to improve the corrosive-resistant properties of less expensive metals, e.g.

20  stainless steel and brass, by the application of Parylene-C polymer film.  This corrosive-resistant coating enables the use of less expensive metals as construction materials by making these metals more $BrF_3$ corrosive-resistant.

25  For safety reasons, the whole apparatus system is set up inside a ventilated fume hood 180.  The process can be automated in which case controller 190 can control the valves.  Alternatively, the entire process can be manual.

30  The inventors found that the characteristics of $BrF_3$ gas are different than other etchants which have been used.  In order to exploit these characteristics, etching processes are preferably conducted using pulse $BrF_3$ flow etching.  Alternately, continuous flow of $BrF_3$ vapor can

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also be used.  The apparatus as shown in FIG. 1A can be
adapted for continuous flow operation.  Mass flow
controls 195, 197, are positioned to regulate the
5  continuous flow rate of $BrF_3$ and Xe respectively during
continuous flow operation.

However, such continuous flow of $BrF_3$ vapor will
etch silicon very fast which makes the etching difficult
to control.  Also, continuous $BrF_3$ flow has a low etching
10  efficiency.  Continuous flow of $BrF_3$ leaves a significant
amount of unconsumed $BrF_3$ vapor; this vapor can enter the
pump system and may cause safety concerns and pump
corrosion.

The etching process begins by loading the wafers
15  in the reaction chamber 110.  Vacuum subsystem 150 is
used to evacuate both the reaction chamber 110 and vapor
reservoir 120 to below 10 mTorr.  The pressure of the
reaction chamber 110 can be read from pressure gauge 170.
The chamber separation valve 172 is then closed.  Valve
20  174 is opened to inject a fixed amount of $BrF_3$ into the
vapor reservoir 120, e.g., around $10^{-4}$ moles of material,
depending on amount of samples to be processed.  For a
load of five 4 inch wafers, 7 Torr of $BrF_3$ are preferably
used.  The chamber separation valve 176 is then opened
25  to allow $BrF_3$ vapor to enter the reaction chamber 110.
Enough time is given to make sure all the $BrF_3$ vapor
inside the reaction chamber 110 is consumed.  This
reaction time is dependent on the number and size of the
wafer being processed.  Finally, the chamber separation
30  valve 172 is opened and both the reaction chamber 110 and
vapor reservoir 120 are again pumped down.  The above
procedures define one pulse of the etching process.  The
process is continued for each pulse.

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Figure 1B summarizes the steps in one etching
pulse.  In step A, valves 176 and 172 are opened and
valve 174 is closed.  The open valves 176 and 172 allow
5    the vacuum subsystem 150 to evacuate the vapor reservoir
120 and the reaction chamber 110. Step B introduces the
gas-phase etchant into the vapor reservoir.  Valve 174 is
opened to allow the gas-phase etchant to fill vapor
reservoir 120.  Valve 176 is closed to prevent the gas
10   from vapor reservoir 120 to fill reaction chamber 110.
In step C, valve 176 is opened to allow the gas-phase
etchant from the vapor reservoir 120 to fill the reaction
chamber 110.  The valves 174 and 172 are closed to
prevent escape of the gas-phase etchant.  Step D closes
15   valve 176 and valve 172, thereby isolating a controlled
gas-phase etchant atmosphere inside the reaction chamber
110.  Step D lasts for a duration sufficient for all of
the gas-phase etchant to be consumed.  Another pulse is
applied by repeating steps B to D.
20        At room temperature and 6 Torr pressure in the
vapor reservoir 120, the number of $BrF_3$ molecules in one
pulse is calculated to be around $1.29 \times 10^{-4}$ mole.  When
the atmosphere in the vapor reservoir equalizes with
reaction chamber 110, there is  $1.1 \times 10^{-4}$ mole of $BrF_3$ in
25   the reaction chamber 110.  According to the equations (1)
to (5), theoretically up to 2.3 mg of silicon can be
etched away per pulse.


SAMPLE PREPARATION
Silicon etching processes are conducted on silicon
30   dice with edges covered by hard baked photoresist, which
is shown later to have a very low etching rate.  The
material is first prepared to remove the native oxide on
the silicon surface.  The samples are etched in buffered

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hydrofluoric acid for 10 seconds followed by deionized
water rinse and nitrogen drying before etching.  This
removes the native oxide on the silicon surface.  This
5   cleaning step removes the native oxide so that the BrF₃
can react with the silicon surface directly when
introduced in the reaction chamber 110.  Without the
cleaning step, BrF₃ vapors are sufficient to remove the
native oxide.  Once the BrF₃ removes the native oxide then
10  the etchant will proceed to etch the silicon surface.

        Samples are then loaded into the reaction chamber
110 which is evacuated to 10 mTorr.  The samples are then
dried.  A vacuum is applied to vaporize the moisture on
the sample surface.  Samples are maintained under vacuum
15  for at least 10 minutes before starting the first BrF₃
pulse.  This process time under vacuum is also dependent
on the size and amount of wafers to be processed.
Nitrogen gas is then applied to blow away any residual
moisture and contaminants before starting the first BrF₃
20  pulse.  Nitrogen valve 178 and chamber separation valve
176 are opened to introduce the nitrogen gas.

        Nitrogen gas (N₂) drying produces reliable and
repeatable etching.  Baking the sample at high
temperature for drying can also be done but is not
25  necessary.  Acetone cleaning is undesirable.  A white
polymer-like film forms on the silicon surface when
acetone residue is exposed to BrF₃ vapor.  This white film
is undesirable because the film stops further etching.

        The etching depth and the undercut can be
30  measured, e.g. using a microscope with a calibrated
focus.  The thickness of the mask layers before and after
the etching is determined using a Nanospec thin-film
thickness measurement instrument, available from
Nanometrics, Sunnyvale, CA.  The roughness of the silicon

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surface is measured using a surface profiler preferably a
Tencor α-step 200(TM) available from Tencor Instruments.
SEM photographs of surface roughness can be taken;
5 surface roughness are measured by scales on the SEM
photograph.


ETCHING CHARACTERIZATION AND PERFORMANCE
**Bulk Silicon Etching**
10      A first example carries out bulk silicon etching
processes on silicon chips with circular openings.
Single-crystal silicon, Polysilicon, and amorphous
silicon have all been etched effectively using $BrF_3$
containing gas-phase etchant.  The diameter ranges from 4
15 m to 4 mm; other diameters can also be used.  Different
masking materials such as thermal oxide, LPCVD silicon
nitride, hard-baked AZ4400 and AZ1518 photoresist are
used as the mask materials to characterize the etching
rate and etching selectivity.
20      The etching rate of one constant sample opening
with variable gas pressures and constant pulse duration
is measured.  The samples have 800 µm circular window
openings and the constant pulse duration is 10 minutes.
Figure 2 shows the vertical etching depth as a function
25 of the number of pulses at different $BrF_3$ pressures.  The
etching rate ranges from 10 µm/pulse up to 140 µm/pulse,
which correspond to an average etching rate range from 1
µm/min up to 14 µm/min for this particular opening of 800
µm.  The vertical etching depth increases as the number
30 of pulses applied increases.
       The amount of sample etched under various pulse
durations is measured.  The $BrF_3$ pressure is constant at 1
Torr while the pulse duration time is varied from 20
seconds to 20 minutes. Figure 3 shows the mass of silicon

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etched away versus pulse duration time with different
window opening areas.  The samples with different
openings are tested separately.  Figure 3 shows that not
5  only the etching rate but also the system etching
efficiency is a function of exposed silicon area.  The
system efficiency is defined as the ratio of the silicon
mass etched by the system to the theoretical silicon mass
etched assuming all the $BrF_3$ is consumed by silicon, which
10  is 2.3 mg in the preferred system.  The efficiency from
Figure 3 is 80% for a 4 inch (160$cm^2$) bare silicon wafer.

The etching rate as the function of the opening
area is measured.  Circular openings with diameters from
4 µm to 4 mm are used.  All the samples are etched in the
15  same load.  The $BrF_3$ pressure is 1 Torr and the pulse
duration is 15 minutes.  The etching depth and undercut
of these samples versus the sample opening area are
plotted in Figure 4.

Figure 4 shows that the etching depth of the 40 µm
20  to 200 µm samples are about 50% more than the larger
samples.  For the samples with diameters under 40 µm,
smaller openings allow less  silicon to be etched.
Another series of samples are processed with the same
type of samples using 500 mTorr, and 15 consecutive
25  pulses at 1 min./pulse.  All the samples are etched at
the same time.  The results shown in Figure 5 agrees with
the results of Figure 4.

Equation (5) shows that the etching time constant
τ is inversely proportional to the surface area.  The
30  bulk etching process results in Figure 3 indicate such a
qualitative relationship.  Since the $BrF_3$ etched silicon
surface is quite rough, the effective silicon surface
area is larger than the mask opening area A.

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The bulk silicon etching results in Figure 4 and
Figure 5 illustrate the local loading effects for large
openings, e.g. openings greater than 200 μm in diameter.
5  Aperture opening effects are also shown for small
openings, e.g. those under 10 μm in diameter.  These two
effects can be caused by the formation of a local $BrF_3$
depletion region.

The diffusion limited effects can be qualitatively
10  explained by comparing the circular opening radius with
the mean free path L of the gas molecules.  When the
opening radius r is close to L, the diffusion front
profile can be represented by a semi-spherical surface
with radius r, shown as opening A in Figure 6, which has
15  a surface area of $2\pi r^2$.  If r >> L, as in the case of
opening B, it has a surface area of  $\pi r^2$, which means the
number of $BrF_3$ molecules that reaches the silicon surface
per unit area without any collision with other gas
molecules is half of the case A.  This explains why the
20  etching depth per pulse in B is half that of A as shown
in Figure 4.  In the case of opening C, after etch down a
depth of d, when d > 2r, and r << L, the opening that
allows $BrF_3$ molecules enter is reduced compare to the case
of r similar to d, thus reducing the etching rate.

25  **Etching Selectivity**

Checkerboard openings of 800 μm x 800 μm on a
silicon wafer with several masking materials are
processed to characterize the etching selectivity.  The
etching selectivity of silicon to other materials is
30  found to be greater than 3000 to 1 for LPCVD silicon
dioxide, and 1000 to 1 for hard baked AZ 4400 and AZ1518
photoresists.  The etching rate of silicon nitride
depends on the quality and silicon concentration of the

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nitride layer and results in a selectivity range of 400:1
to 800:1.  In the case of most metals, like aluminum,
copper, gold, and nickel, $BrF_3$ forms a passivated

5   non-volatile metal fluoride layer on the metal surface
and further reaction is stopped.  The selectivity over
these metals is greater than 1000 to 1.  The selectivity
of silicon to Polyimide is greater than 1000 to 1.  The
selectivity of silicon to Parylene-C polymer film is

10  greater than $10^4$ to 1.


**Polysilicon Sacrificial Layer Etching**

As shown in Figure 7 and Figure 8, surface
micromachined channels and membranes with silicon nitride
as the structural layer and polysilicon as the

15  sacrificial layer are also released by this $BrF_3$ etching
process.  Figure 9 shows that no obvious etching rate
difference is found among the channels with different
widths.  A total length of 300 μm has been etched into
the channels with 10 etching pulses.  Circular membranes

20  have  similar etching rates as the channels.  The present
invention provides an etch rate that is independent of
the desired geometry of the sample.


**Surface Roughing**

Figures 10A and 10B compare the effect of $BrF_3$

25  dilution on surface roughness.  The inventors found that
the silicon surface etched by pure $BrF_3$ at 1 Torr pressure
is rather rough with about 2μm roughness as shown in
Figure 10A.  When 99 Torr of xenon (Xe) gas is added to
the 1 Torr $BrF_3$, the $BrF_3$ molecules have a much shorter

30  mean free path and are scattered more uniformly under the
higher reaction press.  This effect reduces the surface
roughness to about 0.1 μm as shown in Figure 10B.

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Consistent etching results and high molecular etching efficiency (80%) have been achieved by performing the etching in a controlled pulse mode.  This pure
5  gaseous $BrF_3$ etching process is isotropic and has a high etch rate with high selectivity over silicon dioxide (3000:1), silicon nitride (400-800:1) and photoresist (1000:1).  Gaseous $BrF_3$ etching can also be used in surface micromachining process, where silicon nitride
10  channels and membranes using polysilicon as the sacrificial layer have been successfully fabricated. Gas-phase $BrF_3$ etching is simple, fast, maskable, and repeatable.

Although only a few embodiments have been
15  described in detail above, those having ordinary skill in the art will certainly understand that many modifications are possible in the preferred embodiment without departing from the teachings thereof.  For example, materials other than silicon can be etched in this way.
20       All such modifications are intended to be encompassed within the following claims.

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What is claimed is:

1. A method of etching in micromachining
processes, comprising:
5        obtaining a sample of a material that can be
etched using bromine trifluoride;
        treating said sample by contacting said sample
with a gas-phase bromine trifluoride containing etchant
to produce a desired etch depth in said sample.

10       2.  A method as in claim 1, wherein said treating
comprises introducing a specific amount of etchant into a
chamber with said sample, leaving said etchant in said
chamber for a specified time, and then introducing
another specific amount of etchant in said chamber to
15  define a pulsed operation.

        3.  A method as in claim 2, wherein said sample is
a silicon containing material.

        4.  A method as in claim 1, wherein said treating
comprises storing said etchant as a liquid material,
20  converting the liquid to a gaseous phase, and introducing
the gaseous phase material into an etching chamber.

        5. A method of etching in micromachining
processes, comprising:
25       obtaining a sample;
        treating said sample by contacting said sample
with a gas-phase etchant, for a time defining a portion
of a pulse train, wherein said time lasts for a specified
duration;

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at the end of said time of said specified
duration, stopping contacting said sample with said gas-
phase etchant;

5          repeating said treating for said specified
duration and said stopping, to produce a desired etch
depth.

6. A method as in claim 5, wherein said sample
includes silicon.

10          7. A method as in claim 5, wherein said gas-phase
etchant is bromine trifluoride ($BrF_3$).

8. A method as in claim 5, wherein said specified
duration is when a specified amount of the gas-phase
etchant is consumed.

15          9.  A method as in claim 5, wherein said treating
comprises storing said etchant as a liquid material,
converting the liquid to a gaseous phase, and introducing
the gaseous phase material into an etching chamber.

10. A method of etching, comprising:
20          providing a sample in a chamber;
          evacuating said chamber to a specified level of
evacuation;
          introducing a fixed amount of gas-phase etchant
into said environment;
25          exposing said sample to said gas-phase etchant for
a specified duration;
          removing said gas-phase etchant from said
environment, wherein said introducing, exposing and

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removing forms one pulse of an etching process;

applying a specified number of additional pulses.

11. A method as in claim 10, wherein said gas-
5   phase etchant is bromine trifluoride (BrF$_3$).

12.  A method as in claim 10, wherein said
treating comprises storing said etchant as a liquid
material, converting the liquid to a gaseous phase, and
introducing the gaseous phase material into an etching
10  chamber.

13. A method of etching a substrate, comprising:

obtaining a substrate of a material that can be
processed using semiconductor techniques;

pre-treating said substrate with a cleaning
15  solution which removes a native oxide from a surface of
said substrate;

using a solution including nitrogen to dry said
substrate;

placing said substrate in a sample processing
20  chamber;

introducing a fixed amount of gas-phase etchant at
a determined pressure into said sample processing
chamber;

exposing said sample to said gas-phase etchant for
25  a specified duration;

ending said exposing; and

after said ending, exposing said sample to another
pulse of exposing said sample for a specified duration.

14. A method as in claim 13, wherein said cleaning
30  solution is a solution of hydrofluoric acid.

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15. A method as in claim 13, wherein said solution of hydrofluoric acid is followed by treating with deionized water.

5        16. A method as in claim 13, wherein said gas-phase etchant is bromine trifluoride (BrF$_3$).

17. A method as in claim 13, wherein said cleaning solution is not acetone.

18. An etching apparatus, comprising:

10       a reaction chamber;

a reaction pressure sensor positioned to measure a pressure of said reaction chamber;

a vacuum subsystem positioned to evacuate said reaction chamber;

15       a vapor reservoir coupled to said reaction chamber;

a vapor pressure sensor positioned to measure a pressure of the vapor reservoir;

a gas-phase etchant source, including bromine

20  trifluoride containing gas, therein positioned to feed gas-phase etchant into said vapor reservoir and reaction chamber;

an etchant controller, positioned between said etchant source and said reaction chamber, operating to

25  selectively allow said bromine trifluoride gas to enter said reaction chamber; and

a valve positioned to regulate an inflow of gas from said gas source to said vapor reservoir and from said vapor reservoir to said reaction chamber.

30       19. An apparatus as in claim 18, further

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comprising a sample drying gas source positioned to feed
sample drying gas into said vapor reservoir.

20. An apparatus as in claim 19, wherein said
5  sample drying gas includes nitrogen.

21. An apparatus as in claim 18, further
comprising a xenon dilution system positioned to feed
xenon into said vapor reservoir.

22. An apparatus as in claim 18, wherein said
10  reaction chamber and said vapor reservoir are coated with
a corrosion resistant coating.

23. An apparatus as in claim 22, wherein said
corrosion resistant coating is an organic film, e.g.
Parylene-C polymer film.

15        24.  An apparatus as in claim 18, wherein said
etchant source stores a liquid phase etchant which is
converted to a gas.

25. A method of etching in micromachining
processes, comprising:
20        obtaining a sample;
        treating said sample by contacting said sample
with a gas-phase bromine trifluoride etchant to produce a
desired etch depth, wherein said gas-phase bromine
trifluoride etchant is diluted with a specified non
25  bromine containing gas at a specified ratio.

26. A method as in claim 25, wherein said
specified gas includes xenon.

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27. A method as in claim 26, wherein said specified ratio is 1 Torr bromine trifluoride to 99 Torr xenon.

5          28. A method of gas-phase etching, comprising:
           obtaining a vapor reservoir and a reaction chamber, wherein said vapor reservoir is coupled to said reaction chamber;
           coupling a vacuum subsystem to said reaction
10  chamber and said vapor reservoir;
           obtaining a gas-phase etchant source, wherein said source is positioned to feed a gas-phase etchant to said vapor reservoir;
           positioning a first valve between said gas-phase
15  etchant source and said vapor reservoir;
           positioning a second valve between said vapor reservoir and said reaction chamber;
           positioning a third valve between said vacuum subsystem and said reaction chamber;
20          placing a sample inside said processing chamber;
           first closing said first valve while opening said second and third valve, allowing said vacuum subsystem to evacuate said reaction chamber and said vapor reservoir;
           second closing said second valve while opening
25  said first valve, allowing said gas-phase etchant to enter said vapor reservoir and preventing said gas-phase etchant to enter said reaction chamber;
           third closing said first valve and closing said third valve while opening said second valve, allowing
30  said gas-phase etchant to enter said reaction chamber from said vapor reservoir;

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fourth closing said second and said third valve,
isolating said gas-phase etchant within said reaction
chamber for a specified duration;

5        repeating said second, third, and fourth closing
in sequence, producing a desired etch depth.


29. A method as in claim 28, wherein said
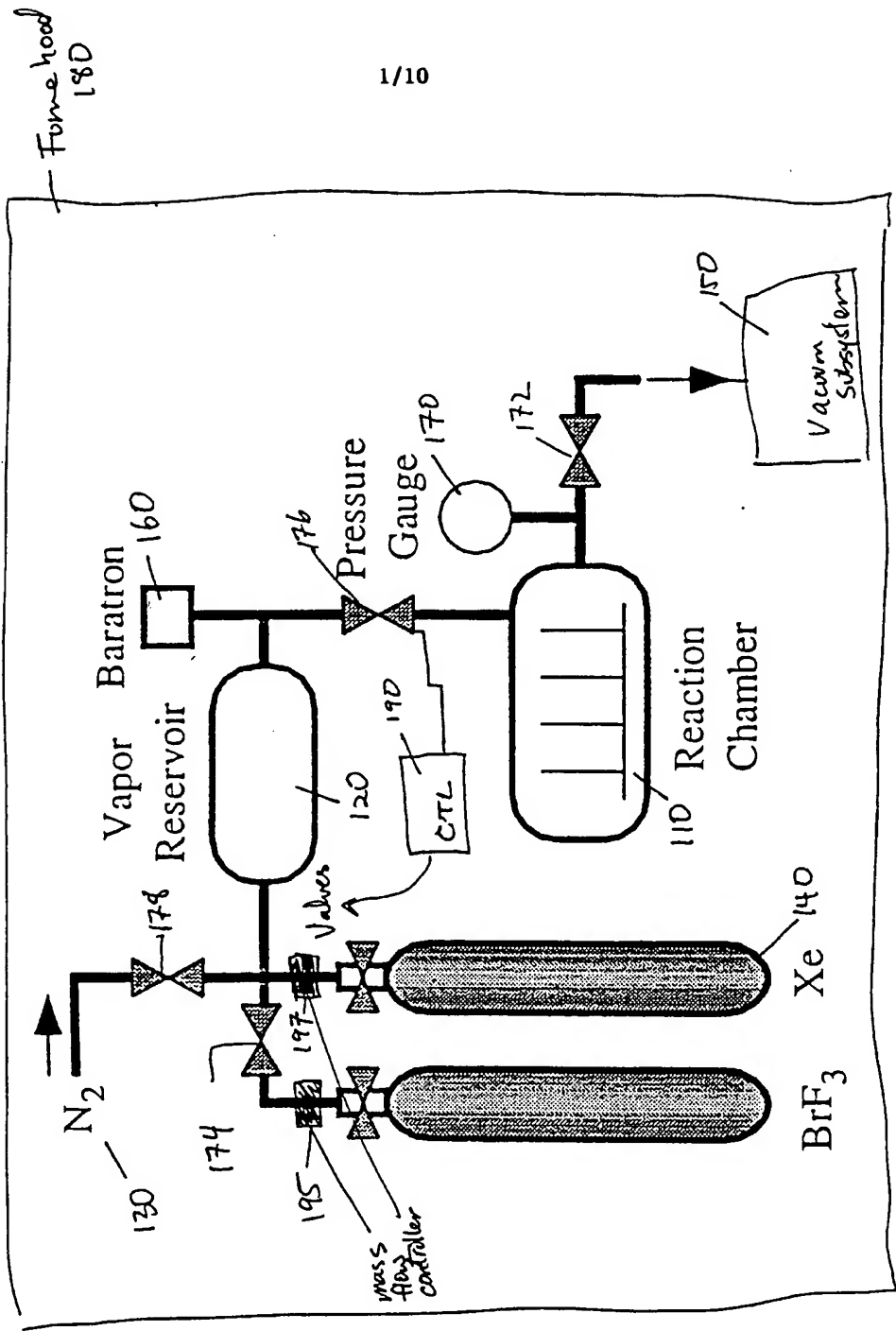specified duration is when a specified amount of the gas-
phase etchant is consumed.

*Figure : Schematic of the Etching System*
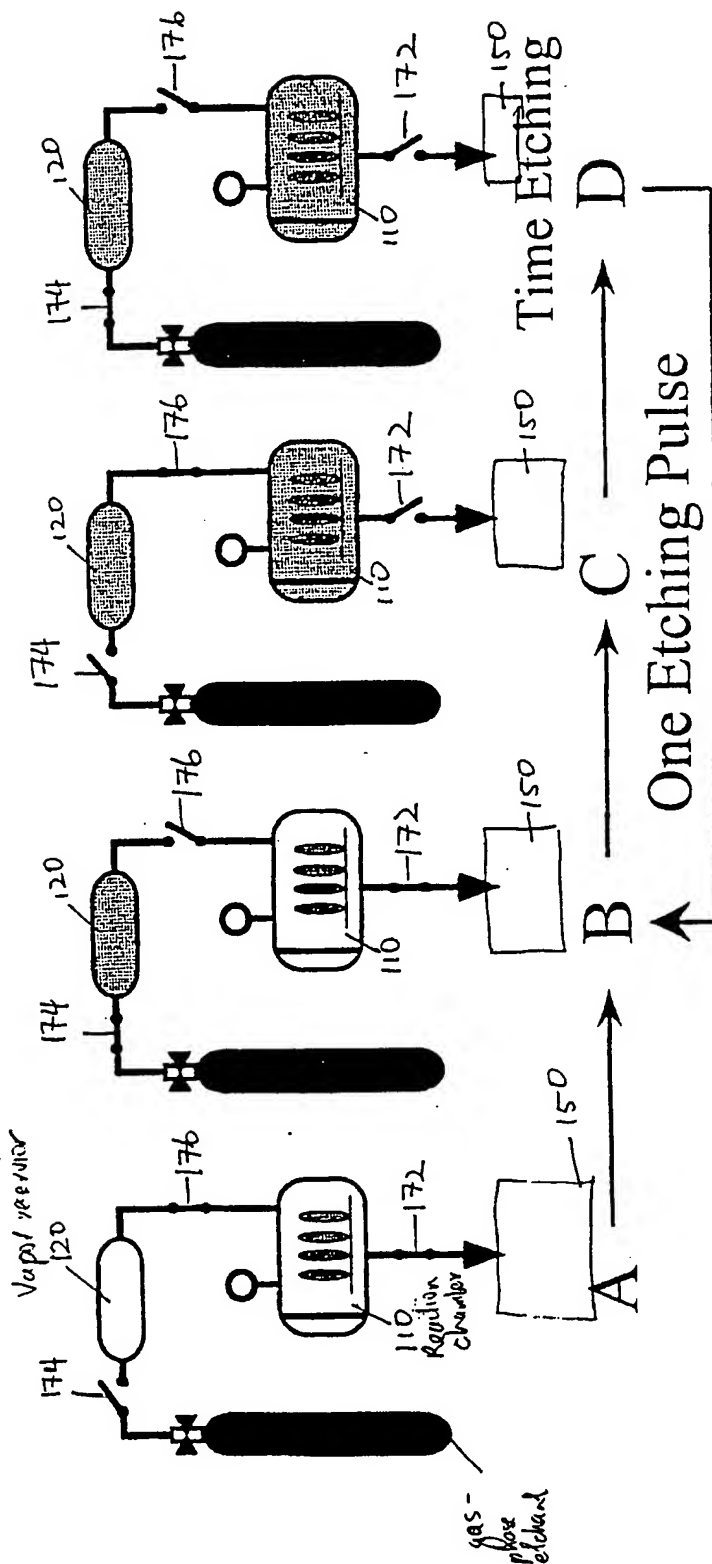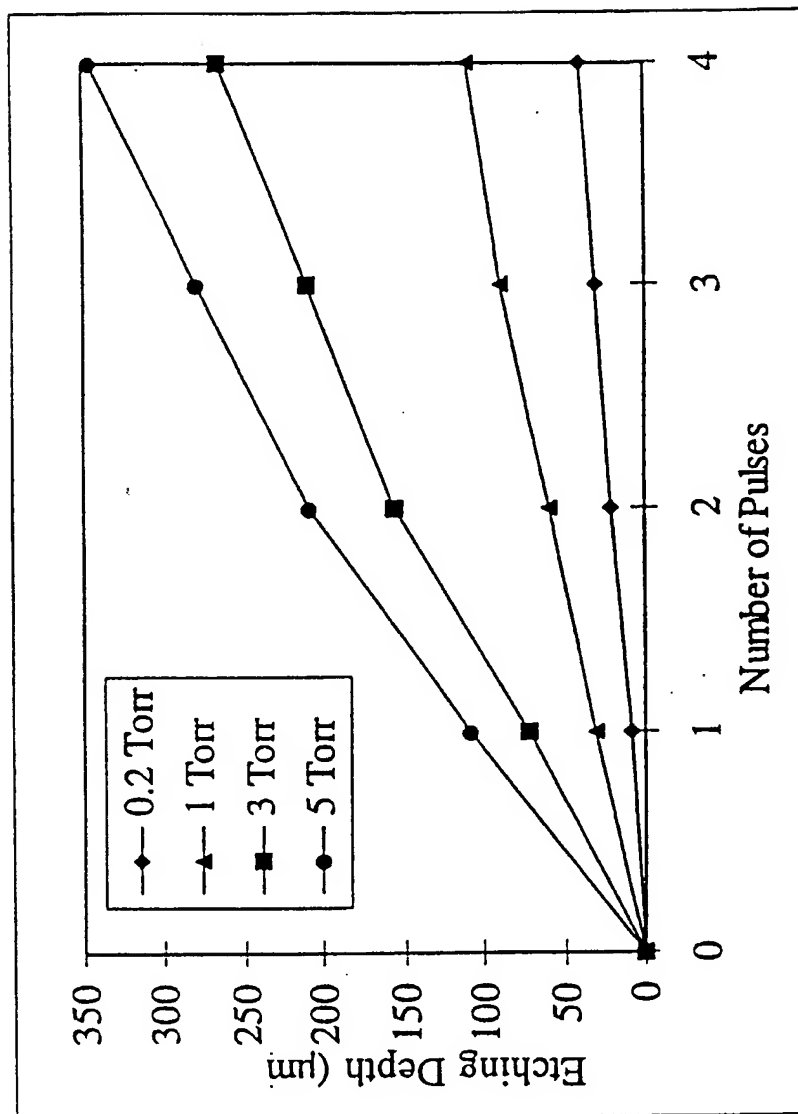*1A*

# Operation

## Definition of One Etching Pulse



Fig.1B

*Figure 2: Etching Rates at Different BrF$_3$ Pressure*
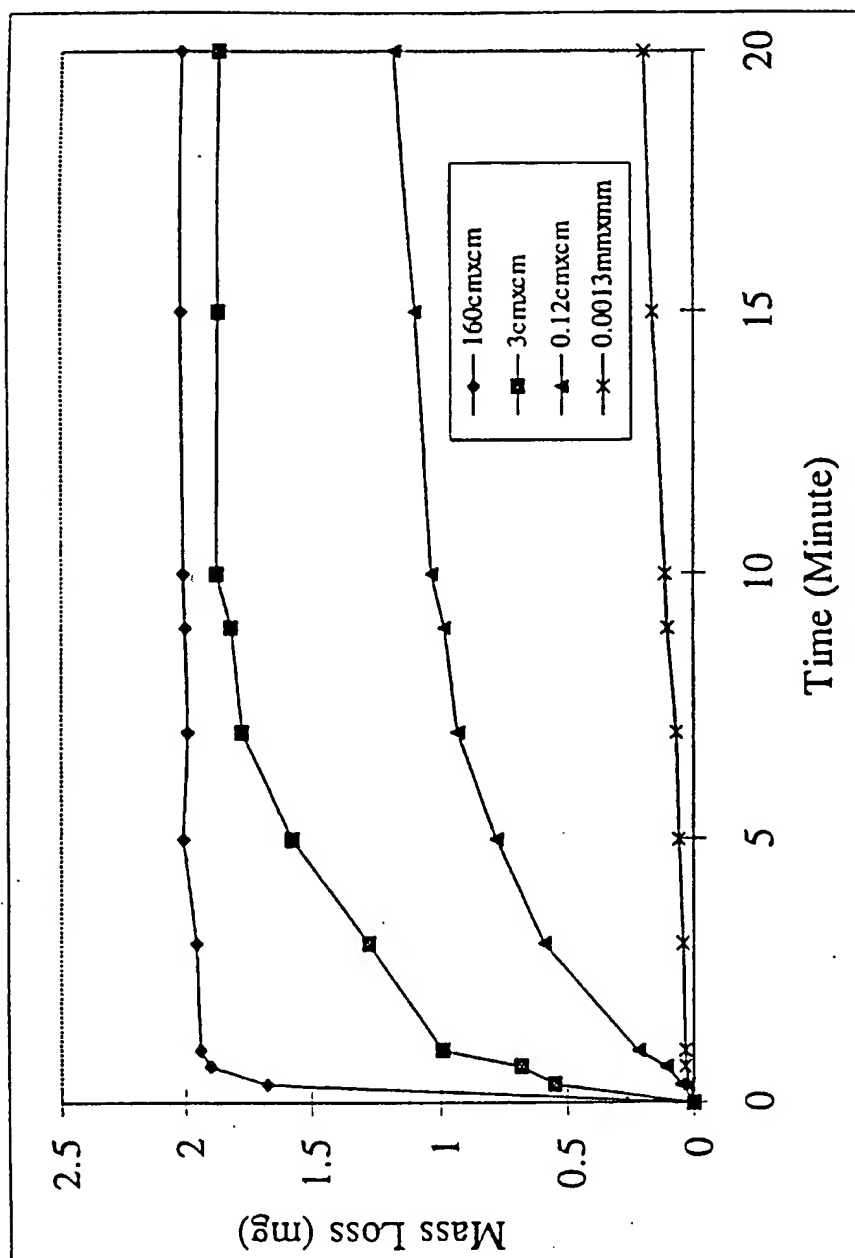
*Figure 3 : Silicon Mass Loss vs. Pulse Duration Time for Different Exposed Silicon Areas*
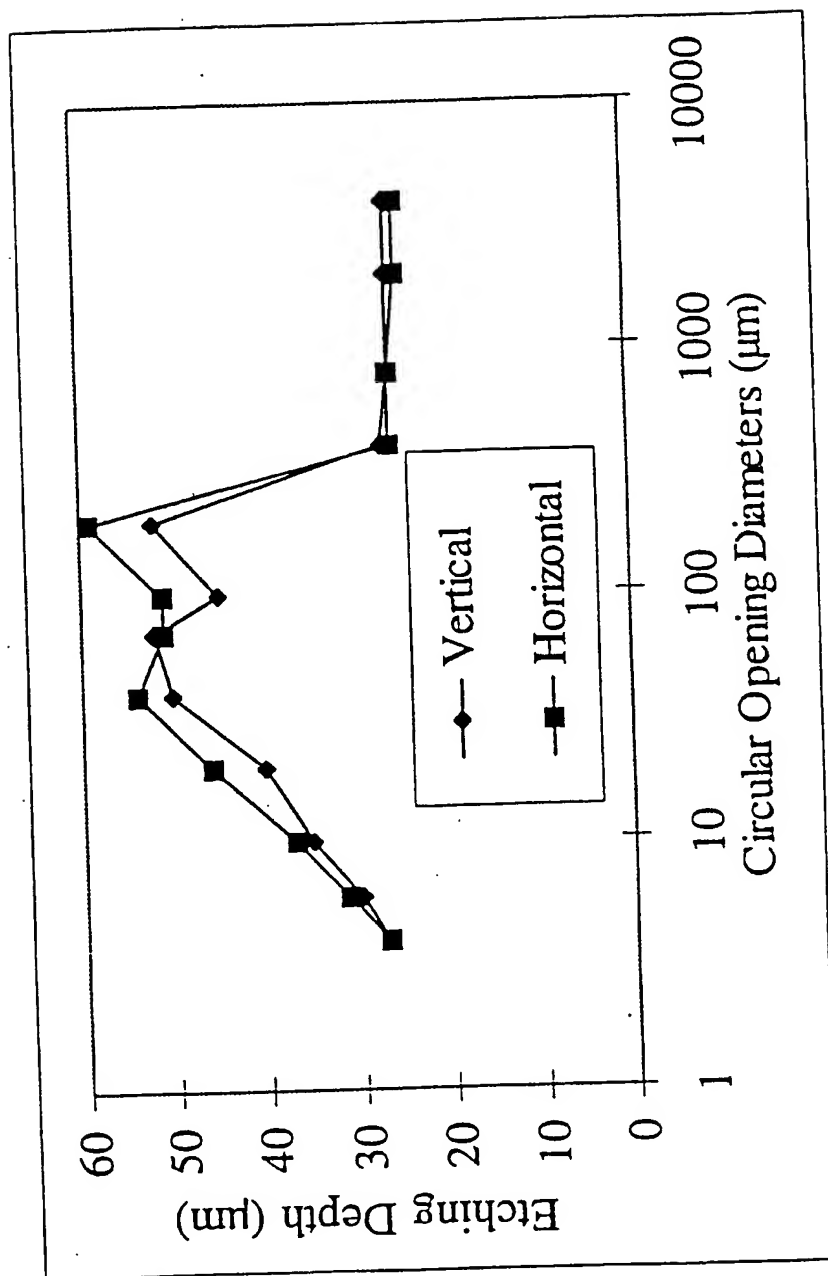
*Figure 4 : Vertical and Horizontal Etching Depth vs. Circular Opening with Diameters of 4µm, 8µm, 10µm, 20µm, 40µm, 70µm, 100µm, 200µm, 400µm, 800µm, 2mm, and 4mm.*
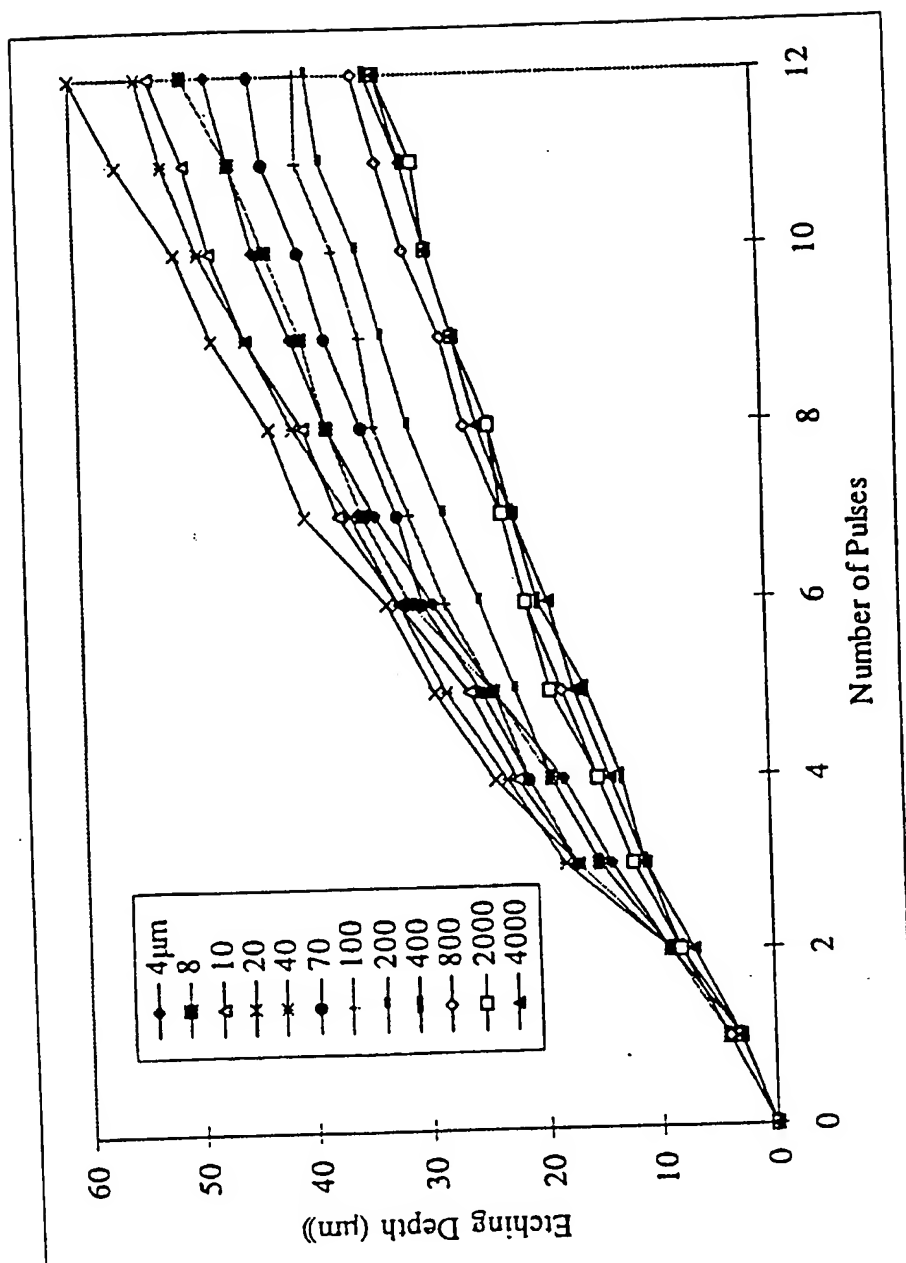
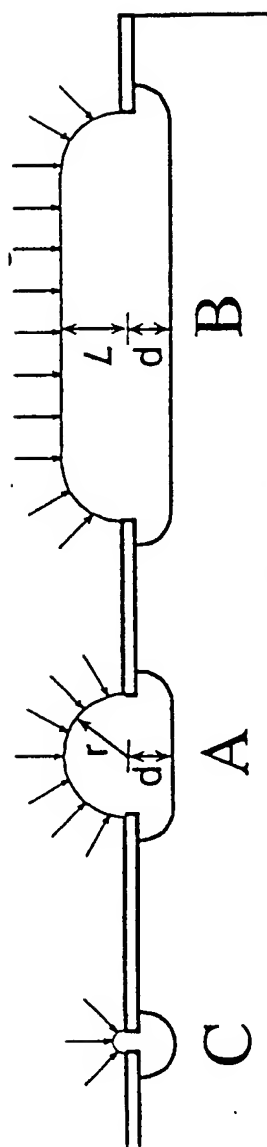Figure 5: *Vertical Etching Depth vs. Number of Pulses with Different Circular Opening Sizes*

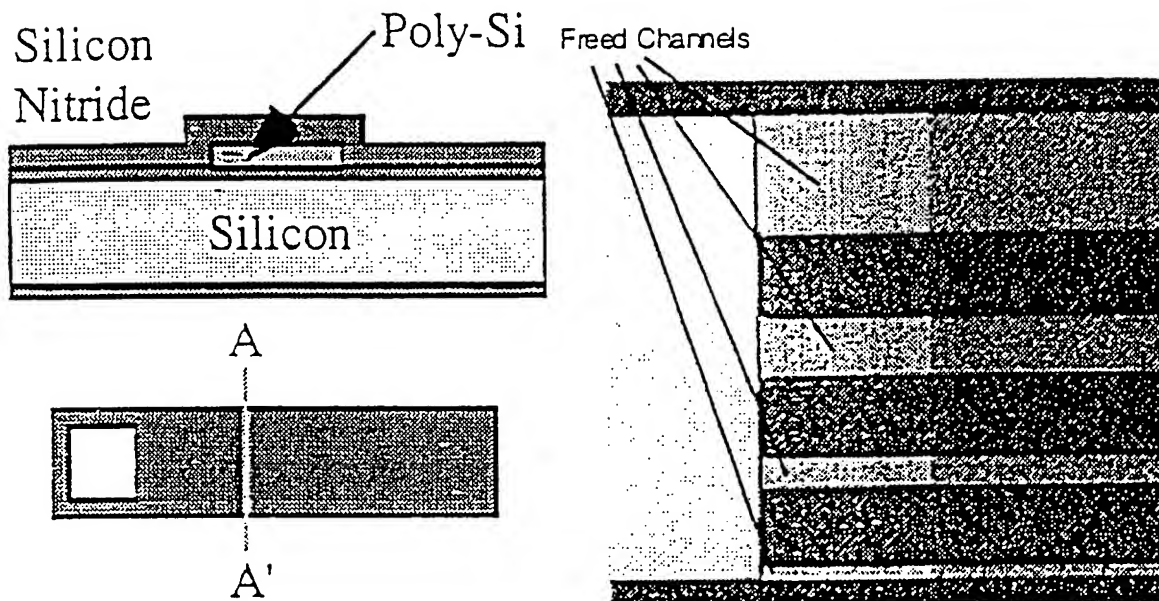Figure 6 : Local Loading Effect and Aperture Opening Effect

Silicon
Nitride

Poly-Si     Freed Channels

Silicon

A

A'

Figure 7: Surface Micromachined Channels

Silicon
Nitride

Poly-Si

Silicon
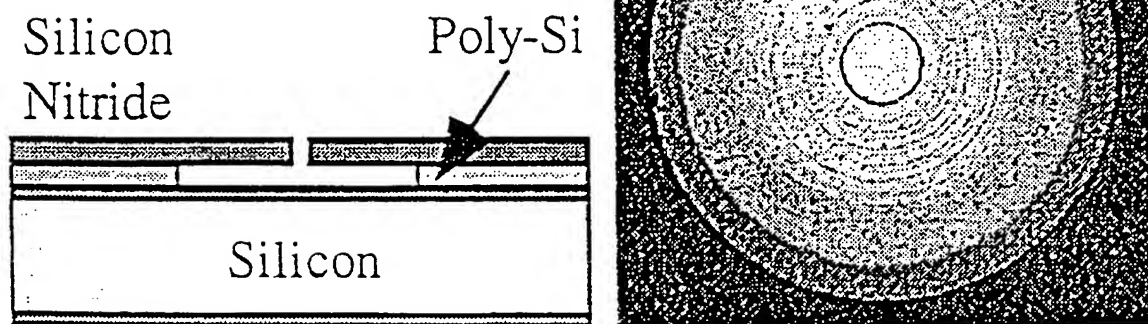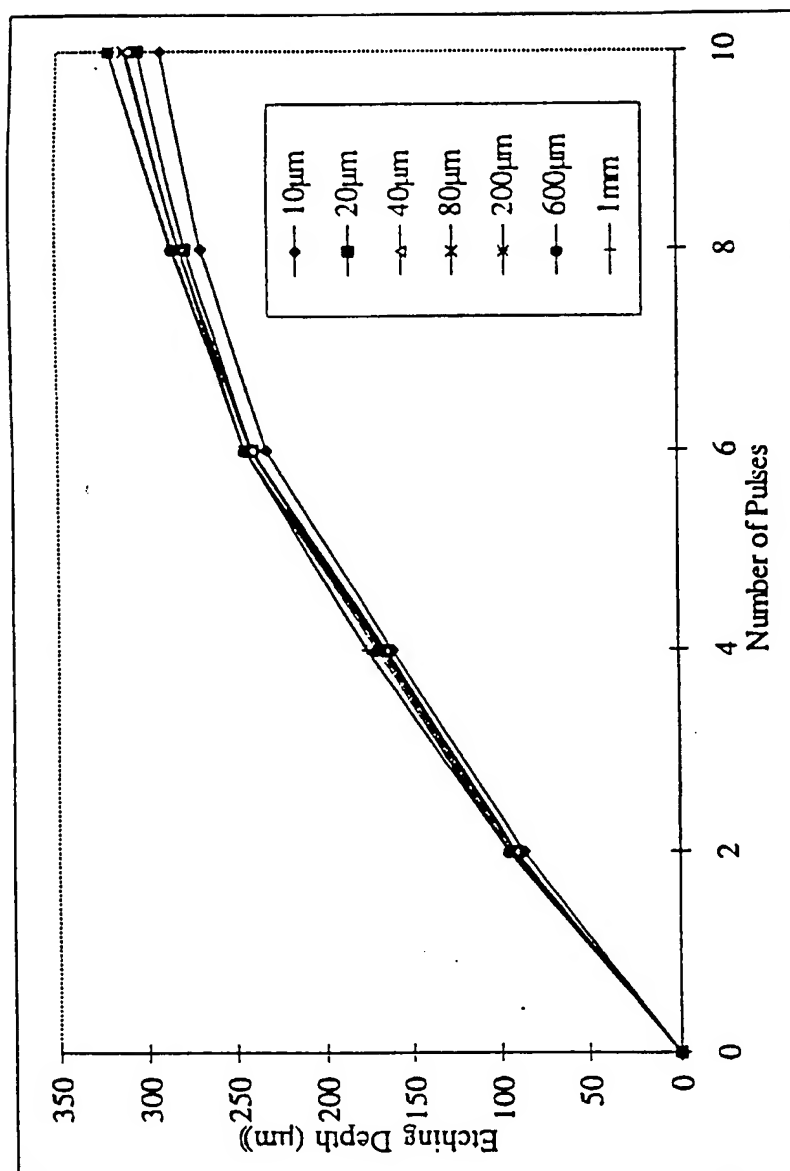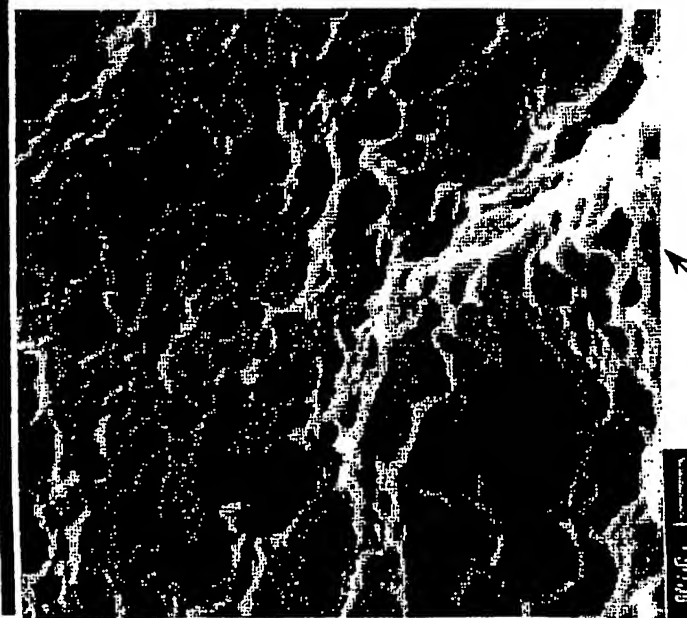
Figure 8: Surface Micromachined Membranes

Figure 9: Etching Length in surface Micromachined Channels vs. Number of Pulses

# Surface Roughness
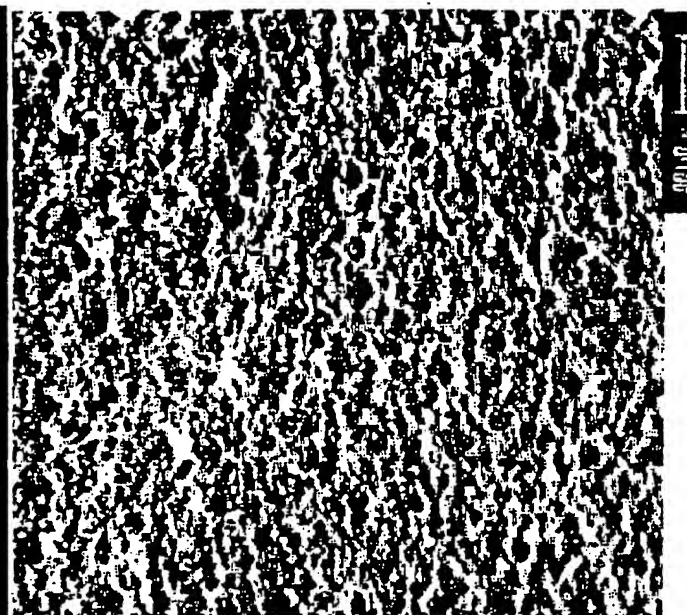


1 Torr BrF$_3$
+
99 Torr Xe

FIG. 10b

1μm

1 Torr
No Dilution

FIG. 10A

International application No.

PCT/US98/01296

## A. CLASSIFICATION OF SUBJECT MATTER
IPC(6) :H01L 21/302
US CL :216/2,49,51,57,64,67,79;438/719,964;156/345
According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 216/2,49,51,57,64,67,79;438/719,964;156/345

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

APS

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | IBBOTSON, D.E. et al. Plasmaless dry etching of silicon with fluorine-containing compounds. J. Appl. Phys. 15 November 1984. Vol.56. No.10. pages 2939-2942, sections II, III.B.2. | 1 |
| Y | | 2-17 |
| X | US 4,498,953 A (COOK ET AL) 12 February 1985 (12-02-85), column 3, lines 17-26, column 4, example 4. | 1 |
| Y | | 25-27 |
| Y | US 4,310,380 A (FLAMM ET AL) 12 January 1982 (12-01-82), column 7, lines 32-38 | 25-27 |
| Y | US 4,749,440 A (BLACKWOOD ET AL) 07 June 1988 (07-06-88), Figure 1, column 6, line 55, column 7, lines 23-33, column 8, lines 15-19 | 18-24 |

[X] Further documents are listed in the continuation of Box C.  ☐ See patent family annex.

| | | | |
|---|---|---|---|
| * | Special categories of cited documents: | "T" | later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention |
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| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 21 APRIL 1998 | 3 0 APR 1998 |

| Name and mailing address of the ISA/US | Authorized officer |
|---|---|
| Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 | ANITA ALANKO |
| Facsimile No.  (703) 305-3230 | Telephone No.  (703) 308-0661 |

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International application No.

PCT/US98/01296

| C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|---|---|---|
| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| Y | US 4,695,700 A (PROVENCE ET AL) 22 September 1987 (22-09-87), Figure 8. | 18-23, 28-29 |
| Y | EP 704,884 A2 (FSI INTERNATIONAL) 03 April 1996 (03-04-96), page 2, lines 46-52. | 2-17,28-29 |

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